Journal Name

COMMUNICATION

Exceptionally Large Two- and Three-Photon Absorption Cross-Sections by OPV Organometalation†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Oligo(*p*-phenylenevinylene)s (OPVs) containing up to 8 PV units and end-functionalized by ruthenium alkynyl groups have been prepared and their nonlinear absorption properties assessed using the Z-scan technique and employing low repetition rate femtosecond pulses. Exceptionally large two-photon absorption (ca. 12,500 GM at 725 nm) and three-photon absorption cross sections (ca. 1.6 x 10^{-76} cm^6 s^2 at 1100 nm) are found for the 8PV-containing example, highlighting the potential of an "organometalation" approach to NLO-efficient organic materials.

Poly(*p*-phenylenevinylene) (PPV) is a π-conjugated polymeric material that displays multiple useful properties such as a significant third-order optical nonlinearity,[1] efficient electroluminescence,[2] and laser emission.[3] However, the lack of solubility of unsubstituted PPV in organic solvents has hampered its processing and therefore its further development.[4] Although various soluble PPV derivatives have been made, it is difficult to modify the structure of the PPV backbone to achieve certain functions. Oligo(*p*-phenylenevinylene)s (OPVs) have therefore been developed as they share some properties with PPV and allow for structural control.[5] Despite the enormous interest in PPV and OPVs, organometallic derivatives of the latter have been curiously little explored, although the ligated metal centres can in principle impart additional desirable functionality (reversible redox properties, strong optical responses, magnetic behaviour, etc.).

The nonlinear optical (NLO) properties of organometallic complexes have attracted significant attention,[6] the most intensively studied examples being metal alkynyl complexes[7] and metallocenyl complexes.[8] Metal alkynyl complexes, in particular, have achieved record values for organometallics of the quadratic (β) and cubic (γ) NLO coefficients, but thus far most studies have focused on dipolar complexes[9] and more recently octupolar (and dendritic) complexes. Relatively few studies have been undertaken exploring the NLO properties of centrosymmetric quadrupolar metal alkynyl complexes, a rare example being oligo(*p*-phenyleneethynylene)s (OPEs) end-functionalized by ligated ruthenium units and containing up to nine PE groups.[10] We were intrigued by the possibility of combining the OPV and metal alkynyl functional moieties, and report herein the syntheses and characterization of OPVs end-functionalized by metal alkynyl groups, together with studies of their nonlinear absorption behaviour that reveal very large instantaneous multiphoton absorption (MPA) cross-sections.

The complexes explored in the present study are shown in Figure 1; complete synthetic details of **1**-**4** and their precursor alkynes are provided in the ESI. The *trans*-

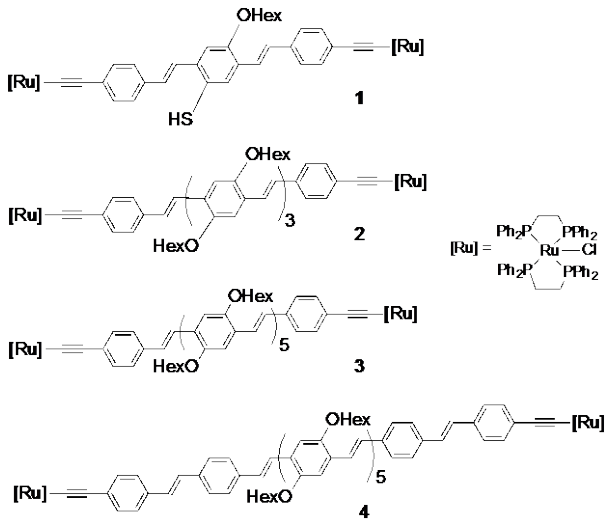

Figure 1. Molecular structures of **1**-**4**. [Ru] = *trans*-[RuCl(κ²-dppe)₂], [dppe = 1,2-bis(diphenylphosphino)ethane].

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† Organometallic Complexes for Nonlinear Optics. Part 56.

Electronic Supplementary Information (ESI) available: Experimental, spectroscopic, and nonlinear optical studies, and NMR spectra. For ESI, see DOI: 10.1039/x0xx00000x

chlorobis{bis(diphenylphosphino)ethane}ruthenium (*trans*-[RuCl(κ^2-dppe)$_2$]) groups that were chosen as the ligated metal peripheral units for this study afford solubility, reversible redox activity associated with strong optical changes, and thermal stability, while alkynyl complexes of *trans*-[RuCl(κ^2-dppe)$_2$] have been shown to possess very large values of the key NLO coefficients.[11] We have previously noted that phenyleneethynylene-based organometallic dendrimers are very soluble in organic solvents due to a combination of dendritic branching and the solubilizing effect of the *trans*-[RuCl(κ^2-dppe)$_2$] moieties.[12] In the present series of complexes, which is PV- rather than PE-based and linear rather than branched, the ruthenium-containing units proved insufficient to solubilize even the 2 PV example *trans*-[RuCl(dppe)$_2$](μ-C≡C-1-C$_6$H$_4$-4-(*E*)-CH=CH-1-C$_6$H$_4$-4-(*E*)-CH=CH-1-C$_6$H$_4$-4-C≡C)-*trans*-[RuCl(dppe)$_2$]; thus, the suite of targeted complexes necessitated incorporation of solubilizing hexyloxy groups in the OPV backbones, and thereby the compositions depicted in Figure 1. Complexes **1**-**4** and the precursor organic compounds were characterized by the usual spectroscopies; complete details are in the ESI. The optical and electrochemical properties of the ruthenium complexes were of particular interest. The cyclic voltammograms of **1**-**4** reveal reversible oxidation processes at ca. 0.56 V (**1**), 0.55 V (**2**), or 0.54 V (**3**, **4**), together with oxidation events at higher potentials with generally lower reversibility; the former are assumed to have a significant metal contribution, by analogy with CV studies on other ruthenium alkynyl complexes,[13] while the latter are assumed to have primarily OPV bridge character. The UV-vis-NIR spectra of **1**-**4** contain low-energy maxima that are primarily MLCT in nature[13] and that red-shift, gain in intensity, and have decreasing metal contribution on OPV bridge lengthening. The low-energy maxima in the UV-vis-NIR spectra of the precursor alkynes **15**-**18** show a similar trend on OPV lengthening. Beyond a critical length, π-system extension has little effect on the spectra of the complexes or precursor alkynes, there being little difference between the spectra of the **3**/**4** and **17**/**18** pairs. Metallation (proceeding from terminal alkyne **15**-**18** to complex **1**-**4**) results in a red-shift and intensity increase in the lowest-energy absorptions, but the red-shift for metallation diminishes on π-system lengthening, supporting the suggestion of a reduction in metal contribution to this key transition. UV-vis-NIR spectroelectrochemical studies on **1**-**4** reveal the appearance of low-energy LMCT bands at ca. 1250 nm on progressive oxidation at 0.8 V.[13] Thus, reversible oxidation of **1**-**4** results in the replacement of strong MLCT bands by intense LMCT bands.

The nonlinear absorption and nonlinear refraction properties were explored using the Z-scan technique[14] over the spectral range 700-1500 nm, and employing low repetition rate (1 kHz) ca. 130 femtosecond pulses to minimize contributions to nonlinear absorption from excited state-absorption. Closed- and open-aperture experiments were undertaken, affording simultaneous evaluation of the spectral dependencies of the absorptive and refractive components of the hyperpolarizability (ESI). Under these conditions, **3** underwent slow photo-degradation, manifested by

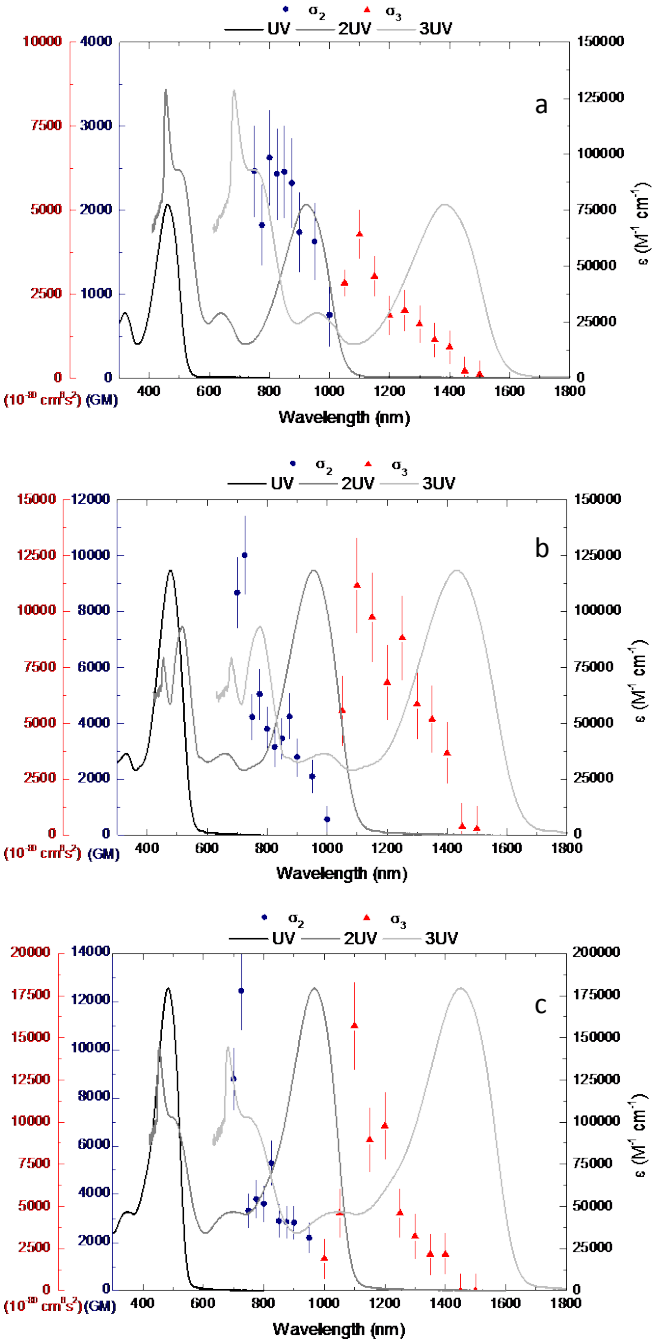


Figure 2. Plots of (a) **1**, (b) **2**, and (c) **4**, showing σ_2 (blue) and σ_3 (red) overlaid on the UV-visible spectrum (black), and including plots of the UV-visible spectrum as a function of twice (dark gray) and three-times (gray) the wavelength.

unsymmetrical open-aperture Z-scan traces and the appearance of a dark precipitate in the cuvette. The degradation was not seen for **1**, **2**, or **4**, and this photo-instability is therefore restricted to the complex with the comparatively most electron-rich OPV bridge. For **1**, **2**, and **4**, the real part of the nonlinearity γ_{real} is negative over the spectral range surveyed. The MPA behaviour of **1**, **2**, and **4** was confirmed to be two-photon absorption (2PA) in the spectral range 700-950 nm and three-photon absorption (3PA) in the spectral range 1000-1500 nm from comparison of the open-aperture Z-scan traces to theoretical fits corresponding to 2PA

and 3PA. The MPA data are plotted in Figure 2, together with the linear optical absorption spectra plotted at twice and three times the wavelength, and the maximal values of the 2PA and 3PA cross-sections are collected in Table 1.

As **1**, **2**, and **4** are centrosymmetric, the 2PA maxima are not expected to correspond to two-times the linear optical absorption maxima, and this is indeed observed (Figure 2). We also note that two-photon excited emission was observed when pumping in the wavelength range 700-900 nm, which is unusual for ruthenium alkynyl complexes, but which may suggest the use of these complexes in possible applications necessitating fluorescence such as multiphoton-excitation-based microscopy (including biological and biomedical imaging) and 3D optical data storage.[15] The 2PA maximal values increase and their location blue-shifts on OPV lengthening, but the increase in maximal value on proceeding from **1** to **2** (with an increase in 2 PV units in the bridge) is considerably greater than the increase in proceeding from **2** to **4** (with an increase in 4 PV units in the bridge), suggestive of the approach of a saturation in this response parameter on OPV lengthening. The 3PA maximal values also increase on OPV lengthening; as with 2PA values, the increase in proceeding from **1** to **2** is much larger than the increase in proceeding from **2** to **4**, again suggestive of approach to saturation, and that further increase in OPV size is unlikely to significantly increase the maximal value.

Table 1. Linear optical and nonlinear absorption cross-section data for **1**, **2**, and **4**.[a]

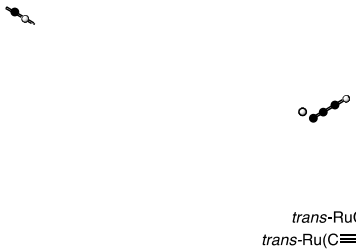
Complex	λ_{max} (nm) [ε (10^4 M^{-1} cm^{-1})]	$\sigma_{2,max}$ (GM[d]) [λ_{max} (nm)]	$\sigma_{3,max}$ (10^{-80} cm^6 s^2) [λ_{max} (nm)]
1 [b]	463 [7.7]	2650 [800]	3500 [1100]
2 [b]	476 [11.8]	10000 [725]	11000 [1100]
4 [c]	484 [18.0]	12500 [725]	15500 [1100]

[a] Measured in CH_2Cl_2 by the Z-scan technique; [b] ca. 0.2% w/w; [c] 0.1% w/w; [d] 1 GM = 10^{-50} cm^4 s.

We note also that the 2PA cross-section has been rigorously shown by Perez-Moreno and Kuzyk to scale quadratically with the number of electrons,[16] so Table 2 also includes scaling by the square of the number of "effective" electrons N_{eff} (i.e., the delocalizable electrons contributing most significantly to nonlinearity: note that we have extended Kuzyk's definition to include ligated Ru atoms, which we have considered as contributing two electrons each, consistent with each metal atom possessing one filled orbital of appropriate symmetry involved in significant overlap with the OPV or OPE π-system).[17] Complexes **2** and **4** are comparable to the performance of these best-performing precedents when scaled by N_{eff}^2.

The 3PA maximal values are exceptionally large for molecules examined with low-repetition rate fs pulses [for a survey of previous reports, see Table S1 in reference 11(b)], while the experimental datum for **4** is a record value from Z-scan studies; the only molecule examined thus far under similar conditions with a similar value of $\sigma_{3,max}$ is the aforementioned nonaruthenium dendrimer based on an OPE

Table 2. 2PA cross-section parameters for **2**, **4**, and related 2PA-efficient complexes.[a]



trans-RuCl(dppe)$_2$ **7**
trans-Ru(C≡CPh)(dppe)$_2$ **8**

Complex	$\sigma_{2,max}$ [b] [λ_{max}][c]	σ_2/MWt [d]	σ_2/N_{eff}^2 [b]	Ref.
2	10 000 [725]	3.33	4.73	This work
4	12 500 [725]	3.28	1.95	This work
5	17 000 [780]	1.46	5.21	11(b)
6	11 500 [750]	1.13	2.48	11(a)
7	18 000 [750]	1.24	2.26	11(a)
8	29 000 [800]	1.23	2.94	11(a)

[a] Maximal values of the 2PA cross-section. N_{eff} is the number of effective electrons, and extending the Kuzyk definition by inclusion of Ru (see text); [b] GM; [c] nm; [d] GM mol g^{-1}.

branched framework (**5**).[11(b)] The only extant σ_3 data similar in magnitude are from three-photon excited fluorescence studies on donor-π-bridge-donor diphenylamino-end-capped oligo(fluorene)s, which have afforded values up to 2720 x 10^{-80} cm^6 s^2 at 1300 nm,[18] and diphenylamino-end-capped oligo(*p*-phenylene)s, for which values up to 45600 x 10^{-80} cm^6 s^2 at 1330 nm have been reported.[19] Table 3 compares the experimental and molecular weight- and N_{eff}^3-scaled σ_3 data for **2**, **4**, and **5**; the ruthenium alkynyl end-functionalized OPV composition is clearly highly efficient.

In summary, end-functionalization of OPVs by chlorobis{bis(diphenylphosphino)ethane}ruthenium alkynyl units has been shown to be an effective strategy to afford molecules with exceptionally large two- and three-photon absorption cross-section values. These cross-sections continue to increase up to the octa(phenylenevinylene)-containing example, but the data are suggestive of approach to saturation, indicating that further OPV lengthening is unlikely to significantly improve MPA merit. These impressive figures-of-merit are maintained when the data are scaled by molecular weight or the relevant power of the number of effective delocalizable electrons contributing to the MPA. The ligated metal end groups in these OPVs endow the complexes with reversible redox activity accompanied by strong optical changes, which in combination are suggestive of the potential for NLO switching.[20] The ligated metal content in these (formally) quadrupolar species is much lower than previously reported metal alkynyl-based dendrimers, suggesting that while metal incorporation affords highly MPA efficient species, it may not be necessary to pursue the higher levels of metalation used in dendrimer construction to achieve

molecules with exceptional multi-photon absorption activity. Finally, the maximal values of these MPA cross-sections occur at different wavelengths from those of highly-efficient previously reported organic molecules, and as putative applications will necessitate activity at specific wavelengths, the organometallics and organics should be viewed as complementary rather than competitive.

We thank the Australian Research Council (ARC), the National Natural Science Foundation of China (51432006), the Chinese Government Ministry of Education, the Chinese Government State Administration of Foreign Experts Affairs (111 Project: B13025), and the National Science Centre of Poland (grant 2013/10/A/ST4/00114) for financial support. M.P.C. thanks the ARC for an Australian Research Fellowship and C.Q. thanks CONICYT (Chile) for a Chile PhD Scholarship Abroad.

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